
REPORT No. 305

**THE GASEOUS EXPLOSIVE REACTION—A STUDY
OF THE KINETICS OF COMPOSITE FUELS**

**By F. W. STEVENS
Bureau of Standards**

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SUMMARY

This report deals with the results of a series of studies of the kinetics of gaseous explosive reactions where the fuel under observation, instead of being a simple gas, is a known mixture of simple gases. In the practical application of the gaseous explosive reaction as a source of power in the gas engine, the fuels employed are composite, with characteristics that are apt to be due to the characteristics of their components and hence may be somewhat complex. The simplest problem that could be proposed in an investigation either of the thermodynamics or kinetics of the gaseous explosive reaction of a composite fuel would seem to be a separate study of the reaction characteristics of each component of the fuel and then a study of the reaction characteristics of the various known mixtures of those components forming composite fuels more and more complex. This is the order followed in the simple studies herein described.

The method and device employed in making these studies were a modification, to meet kinetic principles, of those found so effective by Nernst and his students in investigating the thermodynamics of gaseous explosive reactions. Instead of a spherical bomb of constant volume with central ignition made use of by those investigators, a transparent bomb of constant pressure was substituted. This change eliminated irregularities in pressure and in the mass movement of the active gases during the reaction, and maintained the concentrations (partial pressures) of the active gases constant during the reaction—a feature essential to kinetic studies as well as advantageous in thermodynamic investigations. Further, the substitution of a transparent bomb of constant pressure for an opaque one of constant volume, permitted photographic time-volume records to scale to be secured. From these records it was possible to determine the rate of propagation of the reaction zone in space and, much more important, its rate of propagation relative to the active gases it transforms. As a result of these modifications and their application, it was found that the rate s , at which the zone of explosive reaction moves forward relative to the active gases and effects their transformation is constant, at a constant pressure, and proportional to the product of the partial pressures of the active gases:

$$s = k_1[A]^{n_1}[B]^{n_2}[C]^{n_3}\dots \quad (1)$$

This relationship is the basis of the kinetic studies here made of gaseous reactions, as the equilibrium expression,

$$K = \frac{[A']^{n'_1}[B']^{n'_2}[C']^{n'_3}\dots}{[A]^{n_1}[B]^{n_2}[C]^{n_3}\dots}$$

is the fundamental relation in thermodynamic investigations of gaseous explosive reactions.

The results obtained from the simple specific cases of composite fuels studied would indicate that from a knowledge of the velocity coefficients of the reaction zones of the components of the fuel, the velocity coefficient k_F , of the fuel F , may be determined; and hence the flame velocity of F with O_2 , since

$$s_F = k_F[F]^{n_1}[O]_2^{n_2},$$

where all of the factors to the right in the equation may be known from the velocity coefficients of the components of F and the mixture ratio of F and O_2 .

INTRODUCTION

The introduction to the classical investigations of A. Langen (Reference 1) concerning the pressures generated by the explosive reaction of hydrogen and also of carbon monoxide with oxygen in a bomb of constant volume, contains these words: "The necessary physical basis for the thermodynamic determination of the complete cycle for an internal combustion engine is lacking in many fundamental points. Especially has it been impossible up to the present time to determine with certainty from a knowledge of the composition and condition of the working fluid before the explosive reaction what will be its composition and condition—barring heat losses—after the reaction. This lack in our knowledge so often complained of in physico-technical literature of the past few years was the author's incentive to undertake the present investigation."

In this work Langen repeated and analyzed all of the investigations bearing on these reactions that had previously been made. His publication therefore provides a valuable critical review and summary of the work carried out in investigations of the gaseous explosive reaction up till 1903.

His own investigations were directed to the quantitative determination of the available heat energy imparted to the working fluid of the engine and the changes in composition occurring in that fluid as a result of the transformation; to a determination of the specific heats of the fluid and its final composition as expressed in their reaction constants.

In discussing experimental procedure, Langen strongly emphasized two points: The necessity of employing in investigations of the gaseous explosive reaction a spherical bomb with central ignition; and the necessity of securing a manometer as sensitive as possible and with minimum inertia. The use of a spherical bomb with central ignition was found necessary in order to avoid heat losses due to convection and conduction during the reaction process. The reason that a spherical container with central ignition fulfills this condition is due to the fact that the zone of reaction originating at the center of the bomb, remains concentric with the bomb in its spread outward so that the heated products of combustion inclosed within this expanding spherical shell of flame, do not come in contact with the walls of the container till the end of the reaction and the attainment of maximum pressure. By taking advantage in this way of the symmetry of the gross reaction process, the effect of the container on the heat liberated during the reaction was largely eliminated. Langen was not so fortunate in avoiding significant errors introduced by a material manometer of pronounced inertia and disturbing period.

Recognizing the possibilities of the device and method as demonstrated in the work of Langen, Nernst sought to use it as an instrument of precision in thermodynamic studies of gaseous explosive reactions and in particular for the determination of specific heats of gases at the high temperatures possible to attain by means of explosion methods.

As a result of a long series of trials Pier (Reference 2) developed a manometer that overcame to a large degree the objectionable features met with in previous forms. With this improvement of Langen's device he determined the specific heats of a number of gases. His method has been found applicable for this purpose to temperatures exceeding $3,000^\circ$ absolute and the specific heats of all of the important gases comprising the working fluid of the engine have now been determined at explosion temperatures.

Primarily, a knowledge of the working fluid of an internal combustion engine involves the determination of the equilibrium condition of the fluid under working conditions. The explosion method as developed by Langen and refined by Nernst and his pupils was found particularly suitable to the determination of this constant. The transformation of a hydrocarbon fuel results, for the most part, in the two products of combustion, carbon dioxide and water vapor. These products form an important part of the engine's working fluid. The work of Bjerrum

(Reference 3) and of Siegel (Reference 4), using the explosion method, resulted not only in the determination of the reaction constant K , but permitted also the determination of the degree of dissociation of these important constituents of the working fluid, over wide ranges of temperature and pressure.

Langen, an automotive engineer, expressed the incentive, born of the gas engine, that led to the development of a method and device of high precision and by its aid to the final solution of the fundamental technical problems he sought. This notable advance was wholly due to the rational application of the principles of thermodynamics as extended to gaseous explosive reactions, and to a clear insight and appreciation of the gross mechanism (the spatial propagation of a definite zone of explosive reaction) by which the transformation of the gases is effected. Commenting on these results, Nernst (Reference 5) called attention to "the specially high value that must be attached to the explosion method, since, by suitable variations of the experimental conditions, it enables both the specific heats and the equilibrium constant to be determined." And in like connection, Partington (Reference 6) offers the following: "To the internal-combustion engine designer this knowledge is vital. It is no less important in the determination of explosive forces which are essentially dependent on specific heats of gases produced by explosive material." The determination of the equilibrium constant makes it possible to ascertain the maximal work of the gaseous transformation involved. It thus provides a more rational standard of reference in the analysis of gas engine performance than is offered by an arbitrary standard that takes no account of molecular changes that occur in the working fluid due to reaction, nor to changes in its physical constants due to the high temperatures and pressures at which the fluid is employed.*

A significant result due largely to the effect of these important quantitative studies is that the popular conception of a gaseous explosion is fortunately gradually changing from that of a mysterious phenomenon to that of an orderly normal reaction process well enough understood to be used with precision.

In the list of thermodynamic relations that Langen gave as desirable to have determined in order that a complete cycle for an internal-combustion engine might be followed, another important relation naturally not occurring in a thermodynamic list nor bearing directly on a thermodynamic cycle is, however, from the standpoint of the practical technical application of the gaseous explosion as a source of power, quite as important as a knowledge of the thermodynamics of the reaction. This is a knowledge of the kinetics of the gaseous explosive reaction. (Reference 8.)

Unfortunately, a knowledge of the thermodynamics of the reaction furnishes no insight concerning either the mode or the rate at which the transformation proceeds and the final equilibrium is attained. Nevertheless, the lead indicated by the methods and results of the investigations briefly referred to above determined the device and suggested the method made use of by the writer in kinetic studies of gaseous explosive reactions. Some of the features of the thermodynamic investigations made use of in these kinetic studies of the reaction it is necessary to mention and to show how they were adapted to statistical studies of rates.

In the first place it is clear that the accuracy of the results obtained by Langen and his successors, and referred to by Nernst, depends chiefly on the remarkable symmetry of form automatically assumed and maintained, under favorable conditions, by the gross mechanism of the explosive reaction. In the progress of the explosive transformation, the gaseous system, as pointed out by Haber (Reference 9), automatically falls into three well-defined zones: The region occupied by the initial unburned gases, the zone of explosive reaction marked by flame, and the region of reaction products behind the flame. This latter region, he states, "is not from a thermodynamic standpoint free from oxygen, but from an analytical standpoint it is. In this

* "In the steam-world . . . tables of fundamental data are available in which the numerical results have been evolved by a long process of experiment and of critical sifting by the expert engineer. The user of these tables has confidence in the approximate accuracy of the data and makes extensive application of what he finds in them. With the advent of the internal-combustion engine, no similar information has been available. It is true that incomplete summaries have from time to time appeared, but to the eye of the expert they disclose the most serious inaccuracies and uncritical blunders." (Reference 7.)

region no further burning takes place." It is a region of equilibrium depending on temperature and pressure and expressed by the equilibrium constant,

$$K = \frac{[A']^{n'_1}[B']^{n'_2}[C']^{n'_3}\dots}{[A]^{n_1}[B]^{n_2}[C]^{n_3}\dots}$$

It was this feature that formed the basis of the quantitative determinations of Pier, Bjerrum, and Siegel; they took advantage of the natural symmetry and favorable disposition of the three zones by selecting a spherical bomb fired from the center. At the instant the reaction was complete, the volume, temperature, and pressure of the contents of the bomb were the volume, temperature, and pressure corresponding to the equilibrium constant K . Owing to its symmetrical position within the bomb during the reaction process, the sphere of equilibrium products had suffered a minimum of heat losses.

This most important feature has been retained in the device and methods employed in the kinetic studies made by the writer; it has possibly been somewhat improved upon; for in place of an opaque bomb of constant volume, a transparent bomb of constant pressure (Reference 10) has been substituted, and instead of a material manometer, remote from the seat of reaction, to indicate pressure, direct photographic methods have been employed that permit a continuous and accurate time-volume record of the reaction to be secured. The instant the reaction is complete, the volume, temperature, and pressure of the reaction products are the volume, temperature, and pressure corresponding to the equilibrium constant K . Owing to the symmetrical position maintained within the gaseous system during the reaction, the sphere of equilibrium products, as in the case of a constant-volume bomb, had suffered a minimum of heat losses from the effect of a material container.

The relationship between the thermodynamic results obtained by the bomb of constant volume and the bomb of constant pressure is expressed by the equation of state

$$pv = nRT^*$$

While it is true that from the standpoint of thermodynamics no insight may be obtained concerning either the mode or rate by which the final equilibrium is attained, it is also true that the expression for the equilibrium constant K may be derived also from kinetic principles; that is, this expression may carry both the weight of a thermodynamic law and a deduction from statistical mechanics. (Reference 12.) The expression for the equilibrium constant arrived at either from thermodynamic laws or from kinetic theory is

$$K = \frac{[A']^{n'_1}[B']^{n'_2}[C']^{n'_3}}{[A]^{n_1}[B]^{n_2}[C]^{n_3}}$$

The kinetic relation leading to the above expression is written

$$V = k [A]^{n_1}[B]^{n_2}[C]^{n_3}\dots - k' [A']^{n'_1}[B']^{n'_2}[C']^{n'_3} \quad (2)$$

The experimental application of the above-formulated principles may be illustrated by a particular case—the gaseous reaction



Since the equilibrium condition of a reaction for a given temperature and pressure is independent of the way by which it is attained, it may be assumed that the course of the transformation within the zone of explosive reaction is described by equation (2)

$$V = k [\text{CO}]^2 [\text{O}_2] - k' [\text{CO}_2]^2 \quad (4)$$

and that the equilibrium condition of this process is expressed by

$$K = \frac{[\text{CO}_2]^2}{[\text{CO}]^2 [\text{O}_2]} \quad (5)$$

*"The first attempt at a quantitative kinetic expression is met with in the equation $pv = RT$." (Reference 11.)

Should the reaction proceed almost wholly in one direction, as is usually the case in explosive reactions of gases, the last term in equation (4) may be neglected (Reference 13) and the kinetic expression for the molecular rate of transformation within the reaction zone written

$$V = k[\text{CO}]^2[\text{O}_2] \quad (6)$$

If by some means the successive concentrations of CO and O₂ during the period of transformation from their initial to their final condition, within the reaction zone, could be maintained constant by the introduction into the reaction zone of new initial components *at the same rate* that the reaction products are removed from the reaction zone to the equilibrium zone, then the zone of explosive reaction would represent a constant reaction gradient across it and the relative rate of motion *s* between the reaction zone and the initial gaseous components would remain constant and would express the gross linear rate at which equilibrium was established.

But this imagined process of supplying initial active components to a reaction zone *at the same rate* that the products of equilibrium are formed and removed—an analytical device first made use of by van't Hoff (Reference 14)—is automatically carried out with precision wherever a gaseous explosive reaction is so conditioned that it may run its course in a homogeneous mixture of explosive gases at constant pressure. Observation shows that under these conditions the rate of propagation *s* of the zone of explosive reaction measured relative to the initial active gases remains constant during the reaction and thus expresses the gross constant rate at which an equilibrium is established.

Since the rate of molecular transformation at any instant between the initial and end condition of the reaction process remains proportional to the product of the concentrations of the active gases at that instant, it was assumed that *s*, analogous to *V*, would sustain a like relation to the composition of the explosive gases; the initial composition and concentration of which may be known:

$$s = k_1 [\text{CO}]^2 [\text{O}_2], \quad (7)$$

and since the method employed determines *s* directly,

$$k_1 = \frac{s}{[\text{CO}]^2 [\text{O}_2]}.$$

A further remark in reference to the determination of *k*₁ may be offered here: It seems doubtful if the simplification usually resorted to in the kinetic expression for the rate of molecular transformation occurring at ordinary temperatures and pressures is justifiable in the case of gaseous explosive reactions at high temperatures and moderate pressures. It would seem that in the case of the gaseous explosion (though possibly not for high pressures) the effect of the reverse reaction, represented by the last term in equation (4), would be too significant to be wholly neglected. The degree of dissociation is large for both products of combustion CO₂ and H₂O, at high temperatures and moderate pressures. It may be seen that the effect of this last term in equation (4) is not wholly wanting in equation (7) since it is involved in the determination of *k*₁. The final volume, represented by *r'*, is the actual volume of the products of reaction; it therefore includes the effect of the reverse reaction whatever may be its magnitude; and *r'* is a factor in the determination of *k*₁; for since

$$s = \frac{r^3}{r'^2 t},$$

$$k_1 = \frac{r^3}{r'^2 t [\text{CO}]^2 [\text{O}_2]}.$$

EXPERIMENTAL PROCEDURE

Probably the most familiar example that could be cited of the constant rate *s*, at which the zone of explosive reaction moves forward within the active gases and effects their transformation

under the conditions of a constant pressure, is met with in those numerous cases where a homogeneous mixture of the explosive gases is fed through a tube at a constant time-volume rate and ignited. The zone of continuous explosive reaction then automatically adjusts itself to the rate of gas flow through the tube so that its linear rate of advance relative to the active gases is a constant, s , at any point of the flame surface. If this were not so, the many industrial devices

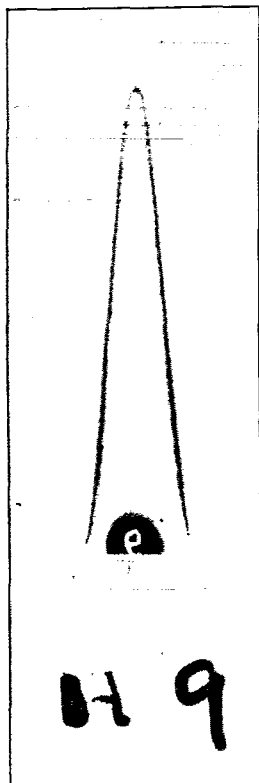


FIG. 1.—Stationary reaction zone formed by the continuous explosive reaction of a homogeneous mixture of CO and $3O_2$ flowing through a tube at a constant time-volume rate. The figure approached that of a cone

based on the reaction as controlled by some form of burner would not be practical. The figure of the stationary reaction zone under these circumstances may simulate more or less closely that of a cone. Its figure would be that of a perfect cone if the rate of gas flow over the entire cross section of the tube were the same and conveniently remained so after leaving the aperture of the tube. Since, however, these velocities vary greatly between the center and the walls of the tube, the figure assumed by the balanced reaction zone becomes, since s is constant, a figure only approximating more or less closely that of a cone.

A photograph of such a stationary reaction zone produced by the continuous explosive reaction of a homogeneous mixture of CO and O_2 as it flows through a tube at constant time-volume rate is shown at Figure 1. The figure represents a cross section of the reaction zone through the vertical axis of the tube. Its form resembles that of a cone.

Under favorable conditions, within rather narrow limits, where the gas flow above the tube may be assumed parallel to the axis of the tube, this figure may be used to estimate the value of s in equation (7); for, between the axis of the tube and its walls, there will exist a zone within which the rate of flow will correspond in value to the time-volume flow u . Assume this zone to meet the flame surface of the zone of explosive reaction at p . (Figure 2.) Then the rate s at which the components CO and O_2 are entering the reaction zone normal to its surface will be

$$s = u \sin \alpha \quad (8)$$

where α is the angle made by a tangent to the curve at p , and the direction of the gas flow assumed parallel to the axis of the tube.

If now a true conical figure be conceived at the top of the tube with the same angle of slant as the tangent at p , and with base the cross section of the tube, then the surface of this cone will represent the surface of a reaction

zone meeting a gas velocity u at all points of its surface, so that

$$s = u \sin \alpha$$

will be true for any position taken.

$$s = \frac{ur}{h},$$

where h is the slant height of the ideal cone and r the radius of the tube. Including equation (7)

$$s = \frac{ur}{h} = k_1 [\text{CO}]^2 [\text{O}_2] \quad (10)$$

An experimental estimate of the value of s in equation (9) was carried out by this device, using flow meters to determine the time-volume rate of flow u , through the tube as well as to determine the composition, in terms of partial pressures, of the CO, O_2 mixtures used. From photographic figures similar to that shown at Figure 1, the values of h were approximated. Some results obtained by the use of this device and method, on the explosive reaction $2 \text{CO} + \text{O}_2 \rightarrow$



FIG. 2

at water vapor saturation, are recorded in Table I and indicated by the mark • in the coordinate Figure 3. In Figure 3 is also drawn the curve, indicated by open circles and a continuous line, of equation (7).

TABLE I

Showing experimental estimates obtained for the rate of flame propagation in the $2\text{CO} + \text{O}_2 \rightarrow$ explosive reaction. Burner method

Record 9-12-22 No.	Partial pressures, atmospheres		Γ [CO ²][O ₂]	$s = \frac{ur}{h}$ (cm/sec)	$k_t = \frac{s}{\Gamma}$
	[CO]	[O ₂]			
1	0.310	0.690	0.0663	45.6	688
2	.350	.650	.0796	55.0	691
3	.395	.605	.0944	66.5	704
4	.405	.595	.0976	72.5	743
5	.425	.575	.1038	70.0	674
6	.425	.575	.1038	71.5	688
7	.440	.560	.1083	78.0	720
8	.440	.560	.1083	79.5	734
9	.460	.540	.1142	78.5	687
10	.460	.540	.1142	88.0	771
11	.465	.535	.1156	82.5	714
12	.480	.520	.1197	84.5	706
13	.490	.510	.1224	84.0	686
14	.495	.505	.1237	89.0	719
15	.505	.495	.1261	91.5	729
16	.515	.485	.1285	89.0	692
17	.520	.480	.1297	93.0	717
18	.535	.465	.1330	89.5	673
19	.545	.455	.1350	90.5	670
20	.555	.445	.1369	99.5	726
21	.590	.410	.1425	101.0	709
22	.635	.365	.1472	103.0	700
23	.665	.335	.1481	102.0	689
24	.695	.305	.1472	103.0	700
25	.745	.255	.1412	100.0	709
26	.865	.135	.1008	75.0	743
27	.870	.130	.0983	67.0	682
28	.870	.130	.0983	57.0	580
29	.885	.115	.0900	58.0	642
30	.895	.105	.0841	50.0	595
31	.900	.100	.0810	46.0	568
32	.910	.090	.0744	41.0	551
Average k_t -----					688

Besides having very narrow limitations, this device at best can give only approximate estimates of the relative motion between the zone of reaction and the active gases entering it. For thermodynamic studies the condition of equilibrium behind the flame may be only approximately determined by the laborious and uncertain method of sampling and subsequent analysis. (Reference 15.)

The symmetry of the spatial propagation of the zone of reaction when running its course within a transparent bomb of constant pressure is, for moderate velocities below the velocity of sound in the gases, very perfect, being that of a spherical shell of flame expanding at uniform rate. Time-volume photographic figures of the progress of the reaction under these conditions are shown in Figure 4. The method by which they are secured has already been described in previous reports. (Reference 16.)

The initial volume of the gases considered is the sphere $2r$ determined by the horizontal diameter of the bubble at the ignition gap. The diameter of the sphere of reaction equilibrium products at the instant the reaction is complete is $2r'$. Since the rate of propagation of the reaction zone is constant during the reaction, its rate in space s' , may be determined at any

instant during the reaction; it is equal to any instant radius, r_t , divided by the time interval t , between ignition and the attainment of r_t ;

$$s' = \frac{r_t}{t} \quad (11)$$

The rate of displacement of the reaction zone measured relative to the active gases is, for a sphere expanding at a uniform rate,

$$s = s' \frac{r^3}{r'^3} \quad (12)$$

Including equation (7)

$$s = s' \frac{r^3}{r'^3} = k_1 [\text{CO}]^2 [\text{O}_2] \quad (13)$$

for the CO, O₂ explosive reaction.

Whether a simple gas is used or a mixture of a number of simple gases, or a gaseous fuel of quite unknown composition, the gross mechanism of the gaseous explosive reaction remains

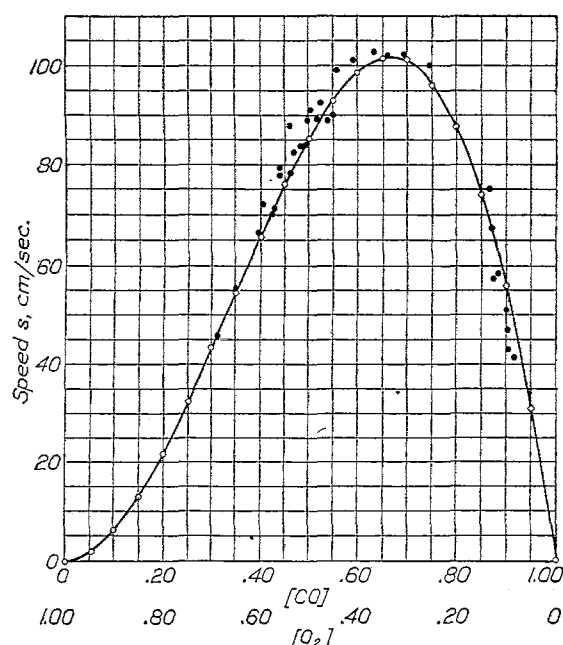
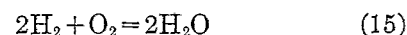
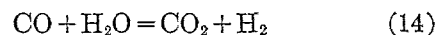


Fig. 3 represents graphically the data given in Table I. The solid circles show observed values, $s = ur/h$. The open circles and continuous line show calculated values, $s = k_1 [\text{CO}]^2 [\text{O}_2]$. Burner method

the same. There is but one zone of reaction in any case. Within this zone the reaction of the explosive gases proceeds to an equilibrium condition of reaction products K . The CO, O₂ reaction here used as example, is not supposed to be as simple as indicated by the conventional chemical equation. The actual transformation is believed to depend upon an intermediate reaction, at least for moderate initial temperatures and pressures. The reaction is supposed to involve an active catalyzer, water vapor, and to proceed within the reaction zone as follows (Reference 17):



yet experimental thermodynamic and kinetic results reveal only the final condition as if the reaction had been simply trimolecular, $2\text{CO} + \text{O}_2 \rightarrow$ with normal maximum for such a reaction,

$$s = k_1 \frac{[\text{CO}]^2}{[\text{CO}]} \frac{[\text{O}_2]}{[\text{O}_2]} \quad (16)$$

The actual microprocess by which the equilibrium K , is attained within the reaction zone can not be expected to be revealed by a method that takes into account the gross rate only at which an equilibrium condition is attained; that is, the rate at which the pressure at constant volume or the volume at constant pressure increases. The microtransformation within the zone may be very complex or comparatively simple, any knowledge of the actual process of it is limited by the present method to what may be drawn from a knowledge of the initial and final condition of the transformation and its gross rate of progress. For instance, in the case under consideration, some insight may be obtained concerning the effect of the amount of water vapor in the initial components upon the rate of propagation of the reaction zone. Drying the gases to a degree below saturation greatly diminishes the value of the velocity constant k_1 . If the gases are dried as much as possible, they will no longer support a zone of explosive reaction at ordinary initial temperatures and pressures.

The fact that the probable intermediate reaction in the case of the CO, O₂ explosive transformation affected only the rate of propagation by its effect on k_1 , suggested the possibility that

the effect of composite fuels on the rate of propagation might be investigated with some success by the constant pressure method. Some results of that investigation are offered in this report.

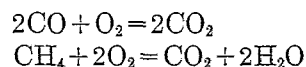
Composite fuels, that will be designated by F, were made up of the gases CO and CH₄ in the following known proportions given in Table II. The characteristics of the explosive reaction of each of the above combinations designated by F were determined over the entire range of mixture ratios of F and O₂ that would ignite and the results tabulated and plotted. Sample records of the results obtained in this study, involving the measurement and calculation of many hundred explosion figures similar to those shown in Figure 4, will be given in this report for those combinations marked * in Table II.

TABLE II

Showing composition of fuel F; the observed and calculated values of k_F , and the composition of F and O₂ for maximum flame velocity, s

Partial pressures in fuel mixtures, F		Partial pressures for s maximum		Observed value k_F	Calculated value k_F
[CO]	[CH ₄]	[F]	[O ₂]		
*1.00	0.00	0.667	0.333	691	-----
*.95	.05	.637	.363	1,113	1,051
.90	.10	.625	.375	1,483	1,364
.80	.20	.557	.443	2,054	1,927
.70	.30	.513	.487	2,476	2,412
.60	.40	.476	.524	2,899	2,829
*.50	.50	.444	.556	3,180	3,189
.40	.60	.417	.583	3,505	3,491
.30	.70	.393	.607	3,794	3,775
.20	.80	.370	.630	4,034	4,031
.10	.90	.351	.649	4,177	4,240
*.00	1.00	.333	.667	4,250	-----

The proportion with which the two gaseous components of F unite with oxygen may be taken as that given in their respective stoichiometric equations:



Then for pure CO and O₂

$$s = k_1 [\text{CO}]^2 [\text{O}_2]$$

The maximum value for s in this equation should be

$$s = k_1 [0.667]^2 [0.333]$$

CO O₂

which is confirmed by experimental results. And from the experimental results, the average value of k_1 was found to be

$$k_1 = \frac{s}{[\text{CO}]^2 [\text{O}_2]} = 691 \quad (17)$$

In Table III are set down the results obtained from the photographic records of this explosive reaction. In the lower curve of Figure 5 is shown the plot of these results, marked ●. There is also shown the complete curve, represented by open circles and a continuous line, of the equation

$$s = 691 [\text{CO}]^2 [\text{O}_2]. \quad (18)$$

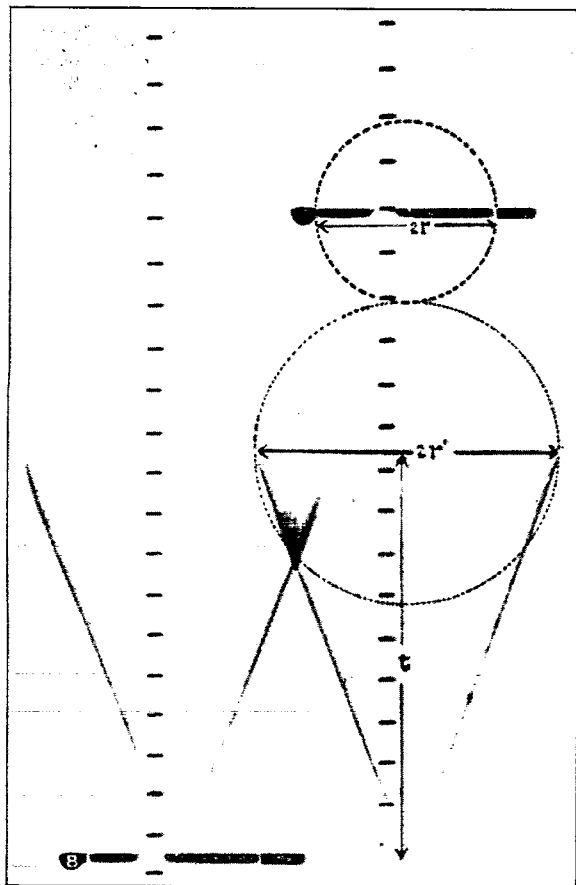


FIG. 4 shows a photographic time-volume record of two gaseous explosive reactions at constant pressure. $2r$ gives the dimensions of the sphere of active gases whose transformation is to be followed. $2r'$ gives the dimensions of the sphere of transformed products at the instant the explosive reaction is completed. The uniform rate of motion, in space, of the reaction zone during the transformation is shown by the slant of the flame trace in the photographic figure. The time intervals shown on the figure are 0.002 second

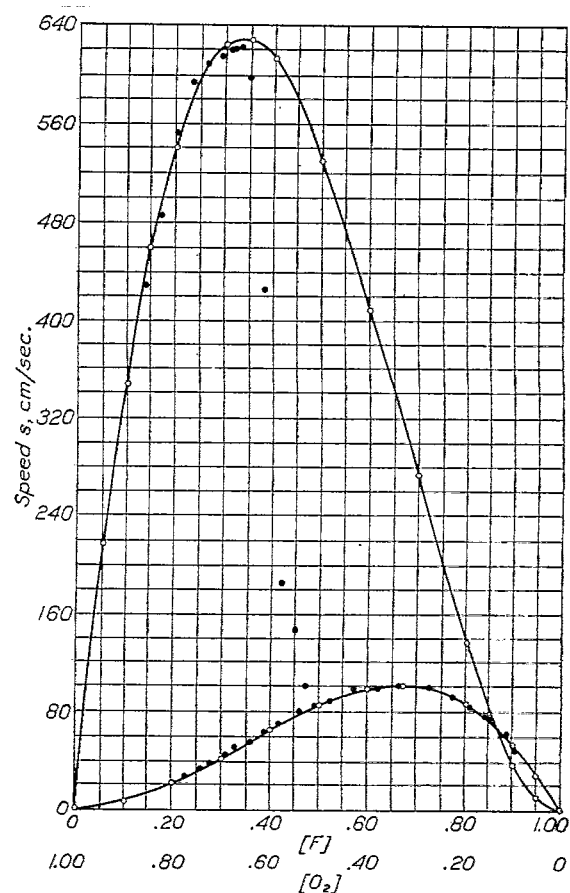


FIG. 5.—The lower curve in this figure represents values of s in the $2\text{CO} + \text{O}_2$ explosive reaction at constant pressure. The solid circles give observed values: $s = s' \frac{r^2}{r'}$. The open circles and continuous line represent calculated values: $s = k_1 [\text{CO}]^2 [\text{O}_2]$. In this upper curve the marks have a like significance except that here they refer to the $\text{CH}_4 + 2\text{O}_2$ explosive reaction at constant pressure

TABLE III

Showing experimental results obtained for the rate of flame propagation in the $2\text{CO} + \text{O}_2 \rightarrow$ explosive reaction. Bubble method

Record 9-7-27 No.	Partial pressure in atmospheres		Γ [CO] ² [O ₂]	$s' = \frac{r_i}{t}$ cm/sec	$s = s' \frac{r^2}{r'}$ cm/sec	$k_1 = \frac{s}{\Gamma}$
	[CO]	[O ₂]				
1-3	0.224	0.776	0.0389	191	27.6	709
4-7	.260	.740	.0500	226	34.7	694
8-11	.279	.721	.0561	279	37.5	668
12-15	.310	.690	.0663	335	45.3	683
16-19	.325	.675	.0713	365	50.3	705
20-23	.359	.641	.0826	434	55.5	672
24-27	.388	.612	.0921	487	63.3	687
28-31	.416	.584	.1011	561	71.1	703
32-35	.460	.540	.1140	632	80.3	703
36-39	.491	.509	.1227	660	84.3	687
40-43	.523	.477	.1305	715	88.4	678
44-47	.574	.426	.1404	794	99.8	711
48-51	.622	.378	.1463	858	100.6	688
52-55	.668	.332	.1480	870	102.8	694
56-59	.726	.274	.1444	849	101.9	706
60-63	.775	.225	.1351	814	92.2	682
64-67	.810	.190	.1247	733	86.4	693
68-71	.840	.160	.1129	632	79.2	701
72-75	.848	.152	.1093	614	77.7	711
76-79	.883	.117	.0912	463	63.9	700
80-83	.903	.097	.0791	320	50.1	633
Average k_1						691

For the methane-oxygen explosive reaction,

$$s = k_1 [\text{CH}_4] [\text{O}_2]^2 \quad (19)$$

the maximum value for s should be

$$s = k_1 [0.333] [0.667]^2 \quad (20)$$

CH₄ O₂

This is found to agree well with observed results, and gives for the average value of k_1

$$k_1 = \frac{s}{[\text{CH}_4][\text{O}_2]^2} = 4,250 \quad (21)$$

The experimental results obtained from this reaction are given in Table IV and plotted in the upper curve of Figure 5. They are indicated by the mark ●. This figure also shows the complete curve, marked by open circles and a continuous line, of the equation

$$s = 4,250 [\text{CH}_4] [\text{O}_2]^2 \quad (22)$$

TABLE IV

Showing experimental results obtained for the rate of flame propagation in the $\text{CH}_4 + 2\text{O}_2 \rightarrow$ explosive reaction

Record 11-21-27 No.	Partial pressure in atmospheres		Γ [CH ₄] [O ₂] ²	$s' = \frac{r_i}{t}$ (cm/sec)	$s = s' \frac{r^2}{r'^2}$ (cm/sec)	$k_1 = \frac{s}{\Gamma}$
	[CH ₄]	[O ₂]				
1-4	0.140	0.860	0.1035	3,347	430	4,155
5-8	.170	.830	.1169	4,536	488	4,172
9-13	.200	.800	.1280	5,156	554	4,326
14-17	.230	.770	.1362	6,048	596	4,375
18-21	.261	.739	.1425	6,098	610	4,280
22-25	.291	.709	.1460	6,359	615	4,212
26-29	.310	.690	.1476	6,586	622	4,212
30-33	.320	.680	.1478	6,636	621	4,200
34-37	.333	.667	.1478	6,714	623	4,213
Average k_1 -----						4,240
38-41	.346	.654	.1478	6,586	598	4,044
42-45	.381	.619	.1457	4,988	426	2,903
46-49	.425	.575	.1411	2,808	188	1,333
50-53	.475	.525	.1308	1,308	102	780

For the case where the composition of the fuel F is 0.95 parts by volume of CO and 0.05 parts by volume of CH₄, the proportion of O₂ necessary to satisfy the conventional formulas of its components for one part F, would be

$$0.95 \text{ CO} + 0.475 \text{ O}_2 = 0.95 \text{ CO}_2$$

$$\frac{0.05 \text{ CH}_4 + 0.1 \text{ O}_2 = 0.05 \text{ CO}_2 + 0.1 \text{ H}_2\text{O}}{1 \text{ F} + 0.575 \text{ O}_2 = 1 \text{ CO}_2 + 0.1 \text{ H}_2\text{O}}$$

and for a tri-molecular reaction,

$$1.91 \text{ F} + 1.09 \text{ O}_2 = 1.91 \text{ CO}_2 + 0.191 \text{ H}_2\text{O}$$

$$s = k_1 [\text{F}]^{1.91} [\text{O}_2]^{1.09} \quad (23)$$

The maximum value of s in this equation should occur for the composition

$$s = k_1 [0.637]^{1.91} [0.363]^{1.09} \quad (24)$$

F O₂

The average value of k_1 found is

$$k_1 = \frac{s}{[F]^{1.91} [O_2]^{1.09}} = 1,103 \quad (25)$$

The experimental results obtained from the explosive reaction of this combination with O_2 are given in Table V and plotted in Figure 6, together with the complete curve for the equation

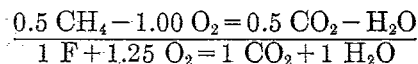
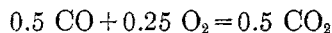
$$s = 1,103 [F]^{1.91} [O_2]^{1.09} \quad (26)$$

TABLE V

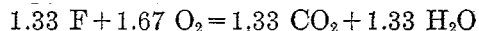
Showing experimental results obtained for the rate of flame propagation in a composite fuel, F, made up of a mixture of 95 parts by volume of carbon monoxide and 5 parts methane, with oxygen

Record 10-11-27 No.	Partial pressures in atmospheres		$\frac{\Gamma}{[F]^{1.91} [O_2]^{1.09}}$	$s' = \frac{r_i}{t}$ (cm/sec)	$s = s' \frac{r^2}{r'^2}$ (cm/sec)	$k_1 = \frac{s}{\Gamma}$
	[F]	[O ₂]				
1-4	0.226	0.774	0.0442	309	48.8	1,007
5-8	.275	.725	.0598	458	65.2	1,090
9-12	.325	.675	.0761	598	85.4	1,123
13-16	.375	.625	.0920	822	103.2	1,123
17-20	.416	.584	.1042	953	113.0	1,084
21-24	.474	.526	.1194	1,150	130.0	1,090
25-28	.527	.473	.1300	1,320	145.0	1,117
29-32	.578	.422	.1371	1,357	154.0	1,124
33-36	.622	.378	.1397	1,434	155.0	1,108
37-40	.676	.324	.1385	1,426	154.0	1,112
41-44	.724	.276	.1326	1,431	146.0	1,101
45-48	.776	.224	.1206	1,296	136.0	1,127
49-52	.818	.182	.1064	1,097	121.0	1,137
Average k_1 -----						1,103

For the case where the composition of the fuel F is 0.5 parts by volume of CO and 0.5 parts by volume of CH_4 , the proportion of O_2 necessary to satisfy the conventional formulas for one part F would be



and for a tri-molecular reaction,

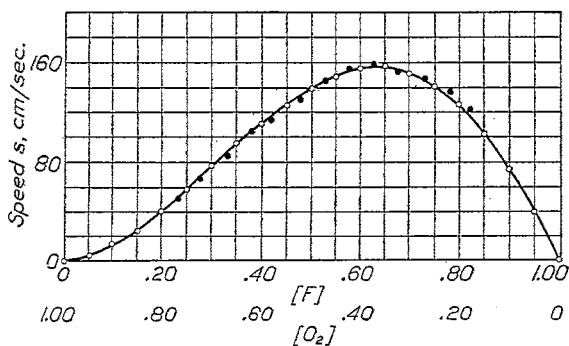


$$s = k_1 [F]^{1.33} [O_2]^{1.67} \quad (27)$$

The average value of k_1 found is

$$k_1 = \frac{s}{[F]^{1.33} [O_2]^{1.67}} = 3,159 \quad (28)$$

Fig. 6 represents graphically the experimental results given in Table V. The values of $s = s' \frac{r^2}{r'^2}$ are shown by solid circles. Theoretical values of $s = k_1 [F]^{1.91} [O_2]^{1.09}$ are shown by open circles and a continuous line



In Table VI are recorded the experimental results obtained from the fuel mixture, 0.5 parts carbon monoxide and 0.5 parts methane, with oxygen. These results, marked ●, are plotted in Figure 7, together with the curve for the equation

$$s = 3,159 [F]^{1.33} [O_2]^{1.67} \quad (29)$$

TABLE VI

Showing experimental results obtained for the rate of flame propagation in a composite fuel, F, made up of a mixture of 50 parts by volume of carbon monoxide and 50 parts methane, with oxygen

Record 11-1-27 No.	Partial pressure in atmospheres		Γ [F] ^{1.33} [O ₂] ^{1.57}	$s' = \frac{r_i}{t}$ (cm/sec)	$s = s' \frac{r^2}{r'^3}$ (cm/sec)	$k_t = \frac{s}{\Gamma}$
	[F]	[O ₂]				
1-4	0.175	0.825	0.0714	1,579	223	3,125
5-8	.225	.775	.0898	2,365	281	3,128
9-12	.275	.725	.1050	2,879	325	3,097
13-16	.325	.675	.1163	3,691	372	3,193
17-21	.375	.625	.1238	4,148	395	3,191
22-25	.425	.575	.1272	4,347	409	3,215
26-29	.473	.527	.1268	4,073	400	3,160
Average k_t -----						3,159
30-33	.485	.515	.1262	3,467	340	2,697
34-37	.498	.502	.1253	3,568	336	2,675
38-41	.508	.492	.1243	3,504	330	2,659
42-45	.521	.479	.1229	3,455	311	2,532
46-49	.532	.468	.1215	3,019	263	2,164
50-53	.555	.445	.1182	2,530	219	1,852
54-57	.606	.394	.1084	1,165	104	956

All of the fuel combinations given in Table II were investigated in the same manner as those described above. The results were tabulated and plotted.

In the coordinate Figure 8 the ordinates represent values of the velocity constants of the reaction zone; the abscissas represent partial pressures of F and O₂. On this figure are plotted the values of k_t against the corresponding partial pressures for maximum velocity of all of the fuel combinations of CO and CH₄ examined. It may be seen from this plot that these k_t values follow closely a straight line drawn between the plotted values of k_{CH_4} and k_{CO} . This would indicate that the values of k_F are simple linear functions of the velocity coefficients of the reaction zone of its components k_{CH_4} and k_{CO} . The slope of this curve expressed in terms of the factors of the gaseous components is

$$C = \frac{k_{CH_4} - k_{CO}}{\frac{n_{CO}}{n_{CO} + n_{O_2}} - \frac{n_{CH_4}}{n_{CH_4} + n_{O_2}}} \quad (30)$$

where the n 's represent the coefficients of the active gases in the respective stoichiometrical equations. Hence

$$C = \frac{4,450 - 691}{0.667 - 0.333} = 11,270 \quad (31)$$

The extension of this curve will cut the y -axis of the coordinate figure at 8206 and the x -axis at 0.728. The value of k_F for any composite fuel made up of any mixture of CH₄ and CO may then be written

$$k_F = 11,270 \left(0.728 - \frac{n_F}{n_F + n_{O_2}} \right) \quad (32)$$

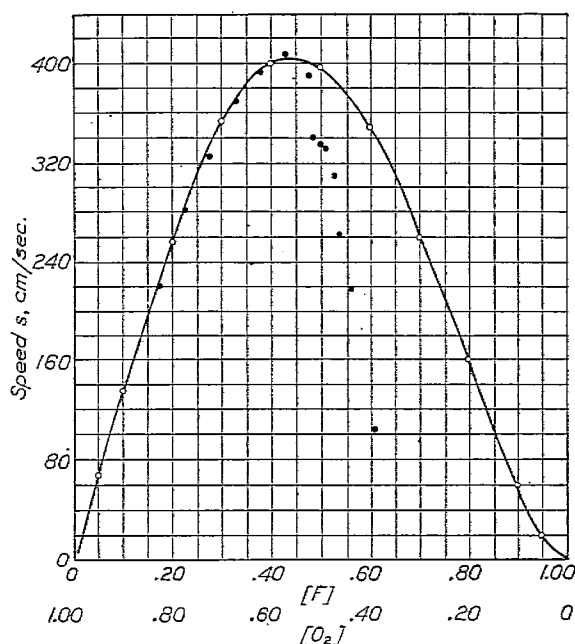


Fig. 7 shows graphically the values obtained for $s = s' \frac{r^2}{r'^3}$ when the fuel consisted of equal parts by volume of CH₄ and CO. Observed values are indicated by solid circles. Theoretical values of s computed from $s = k_t [F]^{1.33} [O_2]^{1.57}$ are shown by open circles and a continuous line

It is therefore possible from a knowledge of the velocity coefficients of the reaction zone of the CH_4 and CO explosive reactions to predict the flame velocity of any composite fuel F , made up of CH_4 and CO ; and that for any mixture ratio of F and O_2 that will ignite, since

$$s = k_F [F]^n; [\text{O}_2]^{n_2}. \quad (33)$$

In the coordinate Figure 9 the curve between the maximal values of $\text{CH}_4 + 2\text{O}_2 \rightarrow$ and $2\text{CO} + \text{O}_2 \rightarrow$ is the locus of the maximal values of s for all possible mixtures of CH_4 and CO with O_2

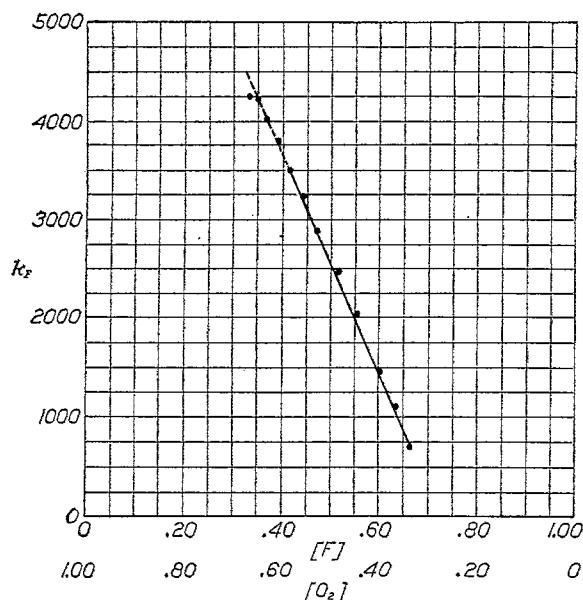


FIG. 8.—The ordinates in this figure represent values of the velocity constants of the reaction zone for those fuel combinations given in Table II. The abscissas represent partial pressures of F and O_2 . The values of k_F in each case are plotted against the corresponding values of $[F]$ and $[\text{O}_2]$ representing the maximum value of Γ .

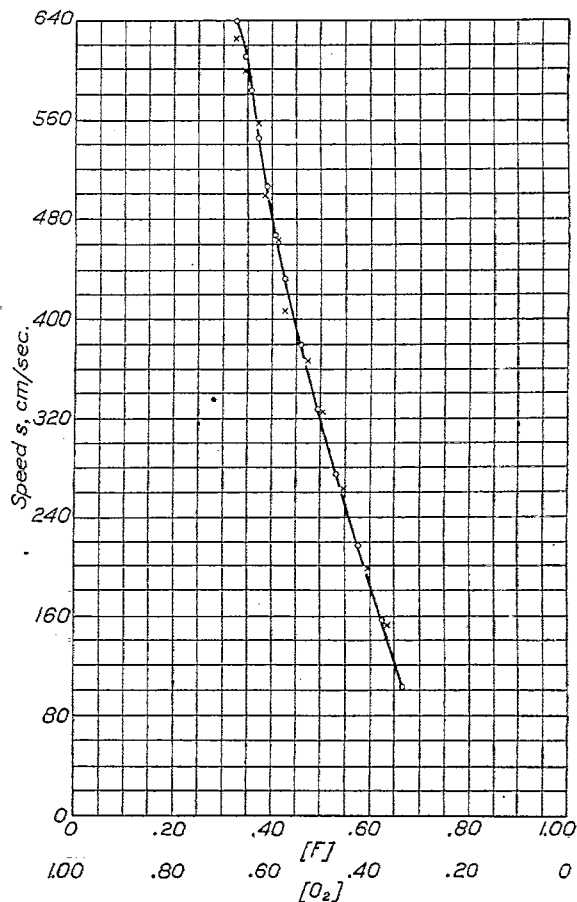


FIG. 9.—The curve represented by open circles and a continuous line in this figure is calculated from equation (33). It is the locus of the maximal values of s for all possible fuel mixtures of CH_4 and CO . The values represented by the mark \times in this figure are the observed maximal values of s found for the fuel combinations given in Table II.

This curve is calculated from equation (33). The points near this curve marked \times are the observed maxima of the fuel mixtures given in Table II.

REMARKS

1. It will be seen by referring to Figure 5 that the observed values of s for the $\text{CH}_4 + 2\text{O}_2 \rightarrow$ reaction no longer follow the curve for equation (22) after passing the point for its maximum value,

$$s = 4,250 [0.333] [\text{O}_2]^{0.667}^2; \\ \text{CH}_4 \quad \text{O}_2$$

and that the deviation of the observed values of s from those given by equation (22) are, for those mixture ratios that will ignite the greater, the greater the excess is of CH_4 over the theoretical amount of O_2 required to oxidize it. This abrupt decrease in the rate of propaga-

tion of the reaction zone—apparently related to the excess of CH_4 in the explosive mixture—may or may not be accompanied by a corresponding decrease in the amount of energy liberated. The constant pressure method employed in these studies permits the determination of the actual work done by an explosive reaction. The constant pressure bomb is an efficient experimental gas engine operating with minimum heat losses and negligible friction against the pressure of its surroundings. The photographic figures shown in Figure 4 are engine diagrams to scale; r and r' represent the initial and final volumes of the reaction. The actual work accomplished by the transformation of a given charge is

$$W = c (r'^3 - r^3)$$

and for unit charge,

$$\frac{W}{r^3} = c \left(\frac{r'^3}{r^3} - 1 \right).$$

In Figure 10 the ordinates of the curve shown are values of $\left(\frac{r'^3}{r^3} - 1\right)$; the abscissas represent partial pressures of the active gases. The figure shows that although the rate of reaction has been greatly reduced by an excess of CH_4 , the total energy liberated has not been affected to the same degree. In fact, the maximum work appears to be obtained with a small excess of the fuel. The rapid decrease in the rate of the explosive reaction, however, due to an increase in the fuel excess, quickly prevents the possibility of maintaining a zone of explosive reaction in the mixture.

2. Composite fuels made up of mixtures of CO and H_2 in different proportions were investigated in the same manner as the CO , CH_4 mixtures that have been described. The results obtained in the two series of measurements differ only in minor details. The reaction of both components, CO and H_2 with O_2 is tri-molecular as it is with CO and CH_4 with O_2 , but with this difference: The maximal value of s in the CH_4 , O_2 reaction (see Figure 5 upper curve) occurs for the combination

$$s = k_1 \frac{[0.333]}{\text{CH}_4} \frac{[0.667]^2}{\text{O}_2}$$

while the maximal value of s for the CO , O_2 reaction (see Figure 5 lower curve) occurs for the combination

$$s = k_1 \frac{[0.667]^2}{\text{CO}} \frac{[0.333]}{\text{O}_2}.$$

The maximal value of s for any mixture of these components will fall intermediate between these values on the curve shown in Figure 9; but the maximal values of s for all mixtures of CO and H_2 will be of the form

$$s = k_F \frac{[0.667]^2}{\text{F}} \frac{[0.333]}{\text{O}_2}$$

and will be arranged about the same vertical axis at 0.667 in the coordinate figures.

3. The range of mixtures of hydrogen with oxygen, and mixtures of hydrogen and carbon monoxide with oxygen, will have greatly differing physical properties as heat conductivities, specific heats, etc. The modifying effect of the physical properties of these mixtures on the

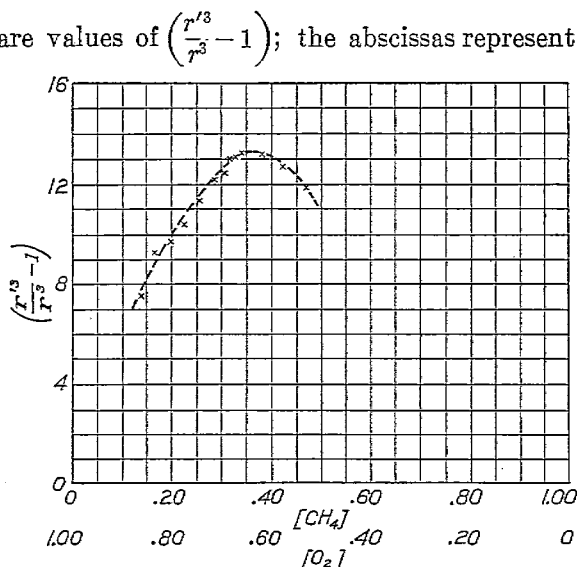


Fig. 10.—This curve shows values proportional to the actual amount of work accomplished by the explosive transformation of unit charge of the various mixture ratios of CH_4 and O_2 that would ignite

rate of propagation of the reaction zone within them is found to parallel similar cases observed and described in Report No. 280 of the National Advisory Committee for Aeronautics (Reference 18).

BUREAU OF STANDARDS,
WASHINGTON, D. C., *April 25, 1928.*

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